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DETERMINATION OF LATENT HEATS OF VAPORISATION OF THE SELENIDES OF CADMIUM AND MERCURY AND TELLURIDE OF ZINC FROM THE ABSORPTION SPECTRA OF THEIR VAPOURS.

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Plates III and IV.

ABSTRACT. From the study of the absorption spectra of selenides of Cd and Hg and the telluride of Zn, their heats of sublimation have been calculated with the help of Born's Cycle. Latent heats of vaporisation for CdSe, HgSe and ZnTe have been found to be 39.40, 83·23 and 61·78 respectively. The difference in the long wave-length limits of continuous absorptions for these compounds has been found to be greater than the atomic term difference $^3P—^1D$ of the electronegative element. This discrepancy have been explained with the help of Frank-Condon diagrams.

INTRODUCTION.

The selenides and tellurides of zinc, cadmium and mercury belong to the same class of diatomic compounds as the oxides and sulphides of these three elements. The absorption spectra of their oxides and sulphides were fully investigated by P. K. Sen-Gupta [1] and given suitable interpretation. In those cases where all the thermo-chemical data are available it is easy to give support to the different theories of photo-dissociation as considered in the case of monoxides and monosulphides. The absorption spectra of only three compounds out of the six are at present submitted and further investigations on the rest are in progress. For these compounds the latent heats of vaporisation have not been determined to the best of my knowledge. It is therefore thought desirable to determine this unknown quantity from the study of their absorption

spectra. It is easily done with the help of the following well-known thermochemical equation.

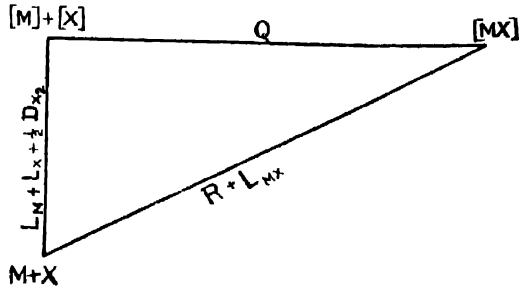

FIGURE 1.

$$L_{MX} = Q + L_M + L_X + \tfrac{1}{2} D_{X_2} - R \quad \ldots \quad \ldots \quad (1)$$

where L_{MX} = Heat of sublimation of the compound [MX]

L_M = ,, ,, ,, metal [M]

L_X = ,, ,, ,, nonmetal [X]

D_{X_2} = Heat of dissociation of X_2

Q = Heat of formation of the compound

R = Atomic heat of dissociation.

The quantity R is known from the long wave-length limit of the first continuous absorption and is connected with the wave-length λ by the equation

$$R = N.\frac{h\nu}{J} = \frac{286000}{\lambda} \qquad (2)$$

All the quantities on the right hand side of equation (1) are known and therefore heat of vaporisation of the compound can be calculated.

In analogy to other similar compounds, the selenides and tellurides may be regarded as ionic in nature, *i.e.*, in the vapour state the compound, for example, cadmium selenide is of the type $Cd^{++}Se^{--}$. When light of a particular frequency say ν_1 falls on the vapour a simultaneous transition of two electrons from Se^{--} takes place to Cd^{++} leaving the products of dissociation in their normal states. Other processes of dissociation may also take place according to the following equations:—

$$MX + h\nu_1 = M + X(^3P) \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

$$MX + h\nu_2 = M + X(^1D) \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

$$MX + h\nu_3 = M + X(^1S) \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

where ν_1, ν_2 and ν_3 are the frequencies of light which dissociate the compound into metal and different states of the non-metal X indicated in the above equations.

EXPERIMENT.

The new modified form of the vacuum graphite furnace is employed to vaporise the three salts for it is found to be extremely serviceable for high temperature work. The furnace in its present form has been fully described elsewhere.[2] The quickness with which it attains a steady high temperature and the ease with which it can be cleaned and manipulated make the furnace extremely serviceable for all such investigations on the absorption spectra of salts melting above a temperature of 600°C. The continuous source of light in the ultra-violet, as usual, was an air-cooled hydrogen discharge tube run by a 2 K. W. high tension transformer. In the visible region, a 40-Watt coiled-coil lamp was employed to obtain a continuous spectral background. For the ultra-violet, a small E_{31} quartz spectrograph and for the visible a constant-deviation glass spectrograph was used. Process plates were used for the ultra-violet and panchromatic plates for the visible spectra. Light from the continuous source passed through the vapour of the salt in the furnace and then allowed to fall on the slit of the spectrograph. At first absorption spectra were photographed at different temperatures. The measurement of temperature was made by a disappearing filment type of pyrometer. It was noticed that without filling the furnace with nitrogen no satisfactory results could be obtained because the vapour of the salt speedily diffused out of the silica tube placed within the current-bearing heated graphite tube. The experiments were repeated several times to obtain the best absorption at the lowest temperature for the three salts separately. After a large number of repititions of the above experiments, the following results were obtained. The positions of different cuts were located with the help of microphotograms. The spot of light was allowed to run over the continuous spectrum which was scratched at different places corresponding to the well-known lines of copper employed as the comparison spectrum. The spot of light was then run over the absorption spectrum. From these microphotometric curves, precentage absorption was plotted against wave-length. The point where this curve cut the wave-length axis gave long wave-length limit of the continuous absorption.

RESULTS.

Cadmium Selenide :—The dark reddish brown powder of CdSe when heated in vacuum from a temperature of 500°C to about 1000°C did not give any satisfactory absorption. On the introduction of nitrogen in the furnace, however, the vapour of the salt gave an absorption spectrum with two cuts with an intermediate region of retransmission as shown in the microphotogram on plate III figure 9. In figures 2 and 3 the percentage absorption curves are plotted which give the positions of the two cuts at λ 3920 and λ 2280. The resonance line of

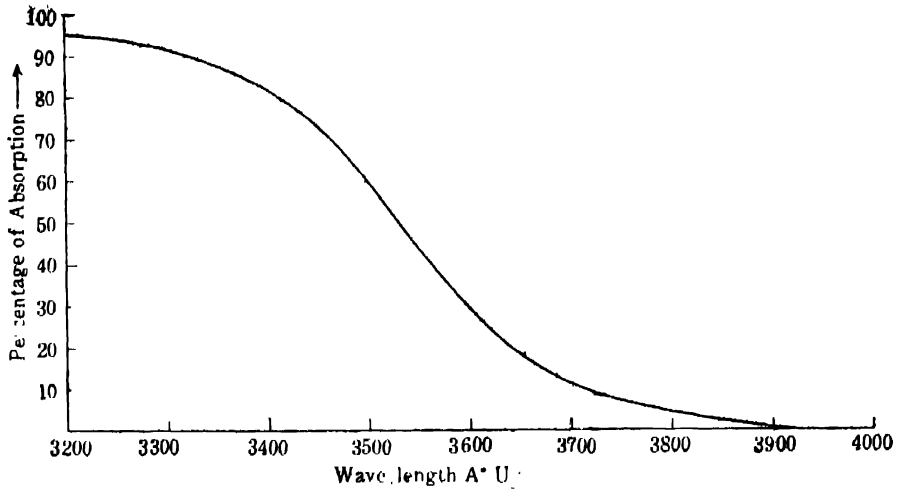

FIGURE 2.

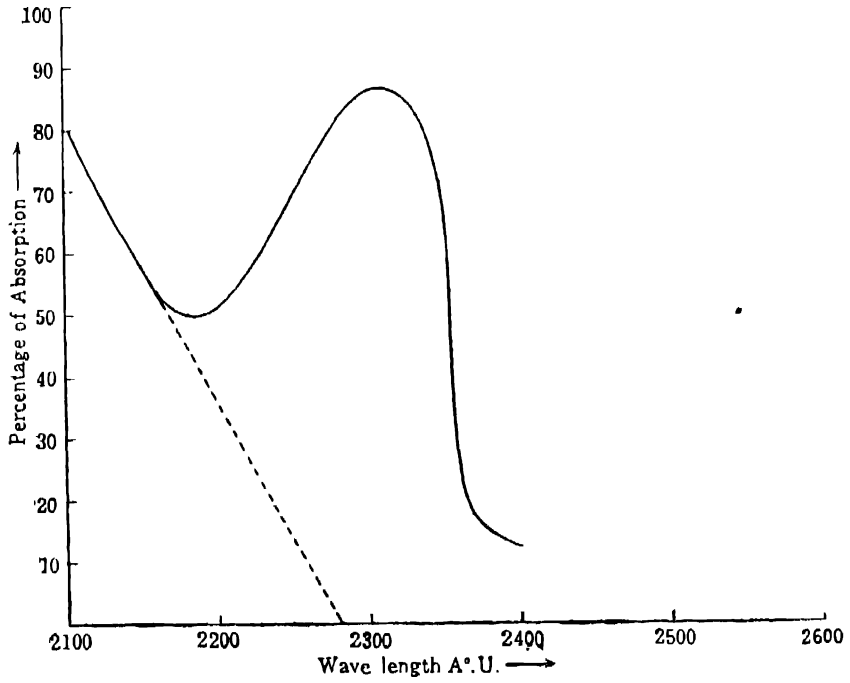

FIGURE 3.

cadmium λ 2288 appeared in nearly all the plates while the intercombination line λ 3261 did come up as it lay in the region of absorption. Usually with the continuous absorption no bands were visible but on those plates where the absorption spectrum was photographed after heating the salt for over 20 minutes, and continuous exposure to the light from the hydrogen discharge tube, Cd_2 bands first obtained by Winans, and confirmed by Sen-Gupta were also observed. Cd line

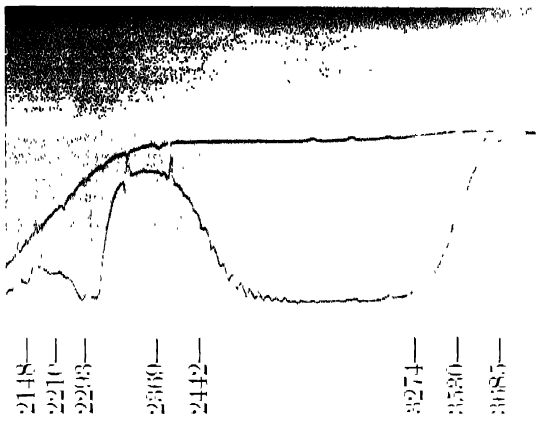

Figure 9
Microphotogram for CdSe

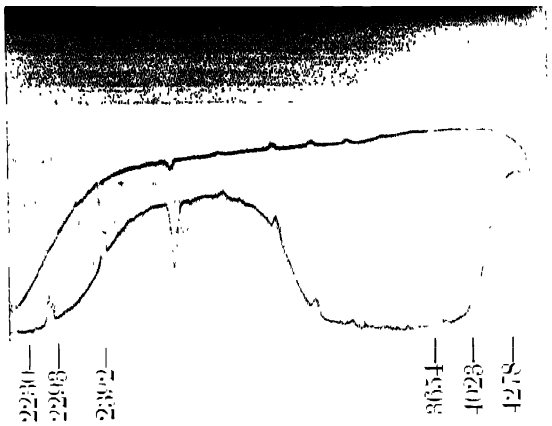

Figure 10
Microphotogram for HgSe

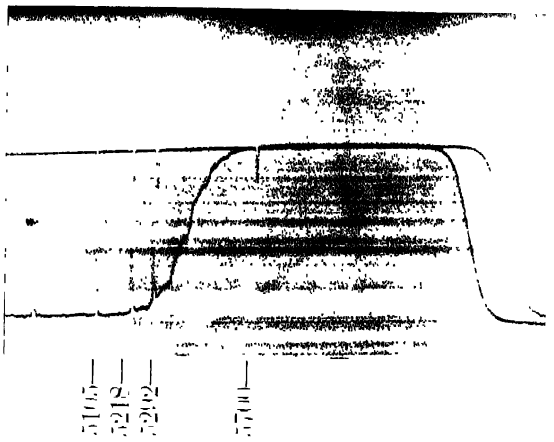

Figure 11
Microphotogram for ZnTe (visible)

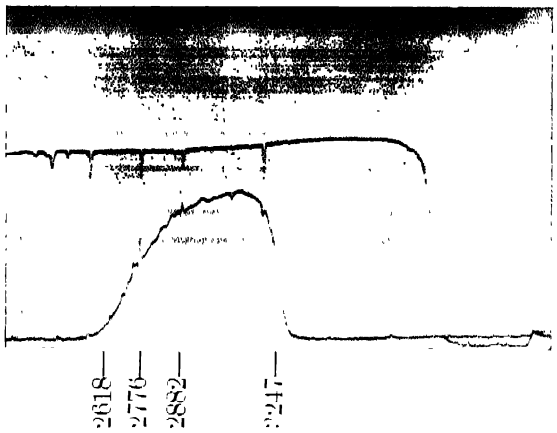

Figure 12
Microphotogram for ZnTe (ultra-violet)

λ 2288 also widened out, at higher temperatures, so much so, that it appeared like a genuine second cut on the plate. Thus in the microphotogram shown in figure 9 the apparent second cut is the broadened Cd-line λ 2288, while the real absorption due to the salt is shown in the last hump.

Mercury Selenide. The vapour of this salt gave a very good absorption spectrum at a temperature of about 820°C. Two cuts were distinctly visible together with the resonance line λ 2536 of mercury. As the temperature was increased the long wave-length limit shifted towards the red. The percentage

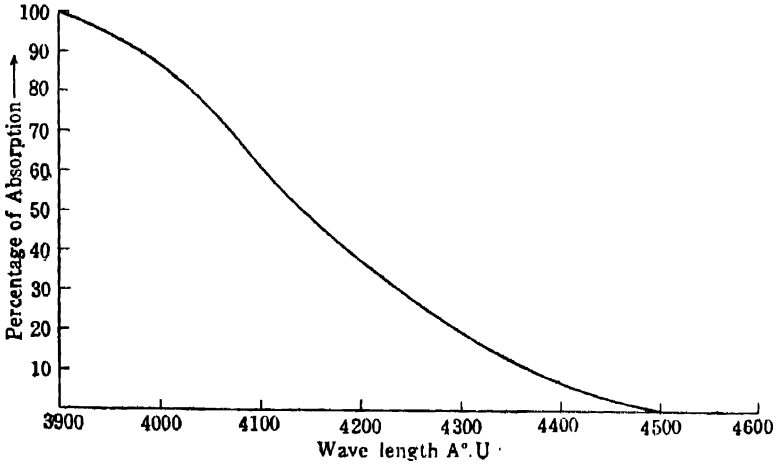

FIGURE 4.

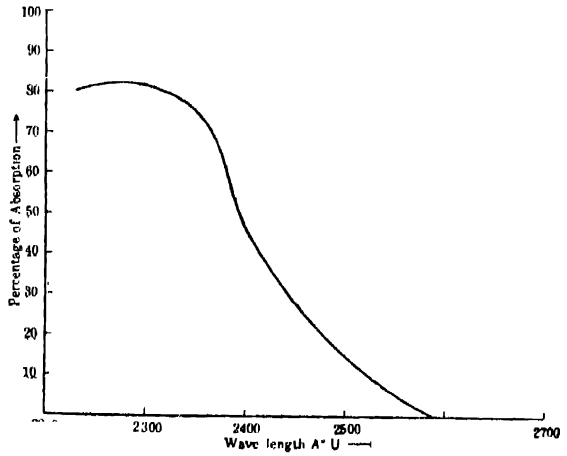

FIGURE 5.

absoption curves for the two cuts shown in the microphotogram plate III are given in figures 4 and 5. It is seen that the long wave-length limits of continuous absorptions in this case are at λ 4500 and λ 2588.

Zinc Telluride. The first cut with zinc telluride appeared at λ 5608 in the visible region while the second cut is located at λ3176. No absorption line or band could be found on these plates. The percentage absorption curves for the two cuts in the absorption spectrum of this compound are shown in figures 6 and 7.

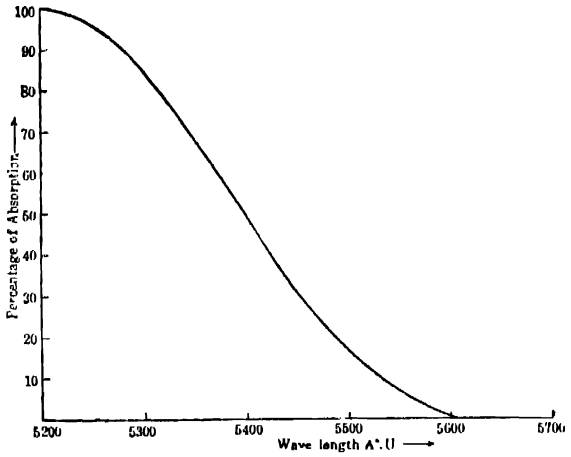

FIGURE 6.

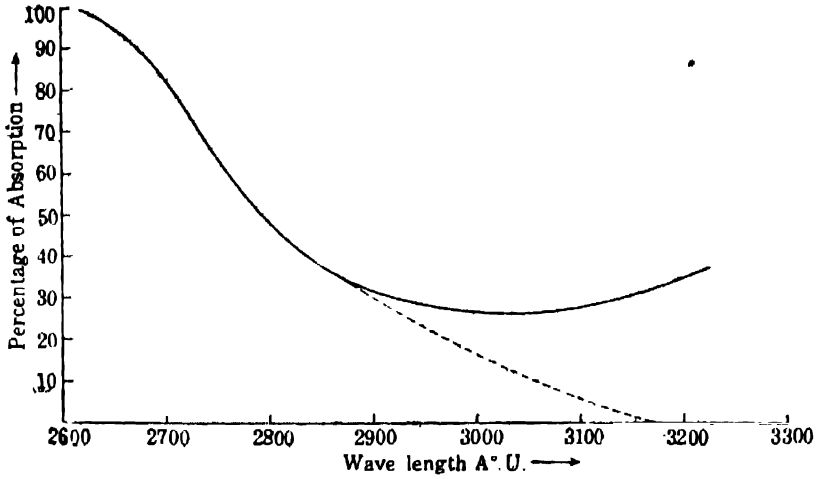

FIGURE 7.

DISCUSSION OF RESULTS.

In table 1 are given the positions of the long wave-length limits of different regions of absorption for the three salts which have been worked here.

TABLE I.

Salt.	I Absorption.		II Absorption.		$h\nu_2 - h\nu_1$.	
	λ A. U.	K. Cal.	λ A. U.	K. Cal.	K. Cal.	e. volts.
CdSe	3920	72·97	2280	125·4	52·43	2·275
HgSe	4500	63·56	2588	110·5	46·94	2·037
ZnTe	5608	51·00	3176	90·05	39·05	1·694

The last column gives the difference $h\nu_2 - h\nu_1$ between the long wave length limits of the two regions of absorption observed for these compounds. This difference has been expressed in K. Cal. as well as electron volts. If the mechanism of photodissociation corresponds to the equations (3) and (4) this difference should be equal to the atomic term difference of selenium for selenides and of tellurium for the telluride. Now, the classification of the arc spectrum of selenium has been thoroughly done by Gibbs and Ruedy [5] and Meissner, Bartelt and Eckstein [6] while atomic term values for tellurium have been investigated by Bartelt.[7] Their term values for the metastable levels $^3P_{2,1,0}$, $^1D_2$ and $^1S_0$ are given in table II together with the differences in electron volts.

TABLE II.

Element.	$^3P_{2,1,0}$	$^1D_2$	$^1S_0$	$^3P_2$-$^1D_2$	$^1D_2$-$^1S_0$
Se	78658·22 76668·73 76123·87	69082·14	56212·19	1·8	1·59
Te	72667 67960 67916	62108	49468	1·30	

The $h\nu_2 - h\nu_1$ differences for the selenides of Cd and Hg as obtained from the absorption spectra are 2·275 and 2·037 electron volts respectively. This value is much larger than the atomic term difference $^3P - ^1D_2$. However, a suitable explanation of this discrepancy can be given as shown in the case of

monosulphides of alkaline earth elements. From the microphotometric and percentage absorption curves it is easily seen that the two regions of absorption are of the same diffuse nature, so that the potential energy curves of the two unstable states are expected to be of the form shown in figure 8.

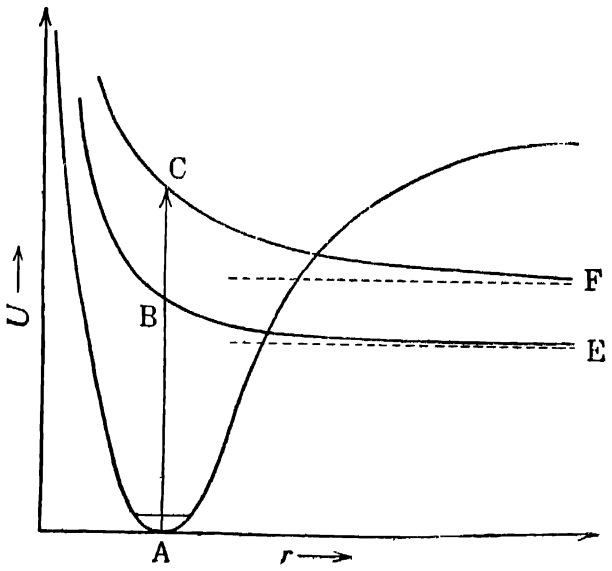

FIGURE 8.

Thus the difference BC is greater than the actual difference EF. The same explanation may also hold for the telluride of zinc where the $h\nu_2 - h\nu_1 = 1{\cdot}694$ while actually it ought to be 1·30.

CALCULATIONS.

As remarked earlier equation (1) furnishes us a means to determine the latent heats of these compounds spectroscopically provided R is calculated from the long wave-length limit of the first continuous absorption corresponding to the dissociation of the molecule into normal atoms. In table III are given the different thermochemical quantities involved in the calculation of L_{MX}.

TABLE III.

Salt.	Q. K. Cal.	D_{X_2} K. Cal.	L_M K. Cal	L_X K. Cal.	R K. Cal.	L_{MX} K. Cal.
CdSe	24·2	44·0	26·77	17·4	72·97	39·40
HgSe	6·3	44·0	15·53	17·4	63·56	83·23
ZnTe	31·0	37·25	31·33	13·2	51·00	61·78

Most of the above data have been collected from Landolt and Börnstein's tables. The heats of dissociation of selenium and tellurium are taken from the paper of Rosen[8] while the latent heats of vaporisation for the element Zn, Cd and Hg are those given by Egerton.[9] The last column of table III gives the latent heats of vaporisation as calculated from equation (1).

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